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An antioxidant and botanical mixture for enhanced sun protection

KEYWORDS: Antioxidants, sunscreen, botanicals, oxidative stability, testing, SPF, PFA, UVA, UVB, argan, bisabolol, tocopherol.

Abstract Formulators are challenged to produce sunscreen products that have a higher SPF to both fulfill consumer needs and to meet the current regulations for these products. Sunscreen actives when incorporated in the correct ratios and with optimal processing can achieve many of the requirements for producing sunscreens. However, other materials exist that are not classified as sunscreen actives and can increase or boost the UVA/UVB protection. Many of these are of natural origin or are derived from plant sources. Antioxidants provide formulators with a wide variety of choices to increase UVA/UVB protection, many of them being of natural origin. Multiple antioxidants have a greater effect than single antioxidants with respect to sun protection.

INTRODUCTION

Ultraviolet radiation from the sun or other sources can cause oxidative damage to the skin from free radicals and reactive oxygen species that form due to the interaction of UV rays with human tissue. This is a major health issue for the population. However, sun damage can also cause aging of the skin in the form of wrinkles, uneven pigmentation, and textural changes that may be related to the loss of moisture or changes within the epidermis. The first layer, the stratum corneum, is responsible for the look, feel, and health of the skin. Sunscreen products that include inorganic or organic actives help to protect the skin from UVA/UVB rays by virtue of their chemical or chemical and physical properties, absorption or reflection.

ANTIOXIDANTS AND BOTANICAL OILS

It is essential not only to protect the skin from the sun, but it is also important to make certain that the skin has essential nutrients available to nourish it. Though the main focus for our study was sun protection with antioxidants we also wanted to be sure the ingredients for our mixture provided skin care benefits, as well. Vitamin E is present within the skin and serves to protect the lipids of the stratum corneum proteins from oxidation. It has been shown to reduce erythema, edema and general oxidation of the skin when applied prior to sun exposure. Vitamin E as tocopherol and its esters have been shown to reduce skin damage from UV radiation. However, Vitamin E Acetate generally needs to be hydrolyzed during skin absorption to show a higher degree of antioxidant activity.

Botanical oils are complex mixtures of natural substances. Many of these contain antioxidants. One of the many materials that we tested successfully was Argan Oil (Figure 1.) which is derived from the kernels of the argan tree (Argania spinosa L.). The oil is composed of unsaturated fatty acids, fatty acids and a variety of antioxidants such as carotenoids, polyphenols, ferulic acid and tocopherols (at about 0.7% as gamma tocopherol). Carotenoids are the most efficient scavengers of singlet oxygen. They are capable of aiding in renewing the cell structure in skin. Vitamin E and carotenoids can be applied topically or taken orally to aid in protection against sun exposure.
As a natural component of plants, polyphenols are all-in-one skincare aids. They are anti-inflammatory, antiseptic and anti-aging. Additionally, they have antioxidant properties, too. These compounds enhance skin growth, protect against sun damage and help the skin hold more moisture. Argan oil contains polyphenols as caffeic acid, oleuropein, vanillic acid, tyrosol, catechol, (-) epicatechin and (+) catechin.

Figure 1. Kernels of the argan tree (Argania spinosa L.) and the flowers of Chamomile (Matricaria chamomilla).

Ferulic acid is the most common polyphenol in argan oil and is believed to be a major component of many plants' self-preservation mechanism. It is effective as a topical antioxidant and its antioxidant potency increases after the skin is exposed to ultraviolet rays, so it is considered beneficial to skin that may be damaged due to UVA, UVB and infrared radiation.
Studies have shown that when ferulic acid is combined with Vitamin E, it doubles the vitamin's capacity as a sun-protective agent and boosts its ability to neutralize free radicals. Argan oil also contains squalene which is a fat-soluble antioxidant.
Argan oil contains the sterols: schottenol, spinasterol and D-7 stigmasterol Sterols are found naturally in the outermost layer of the human skin where they strengthen the skin's photo-protective barriers, improve skin elasticity, improve skin metabolism and help to keep moisture in the skin. They also maintain the structural integrity of the cell membranes in our skin and fend off inflammation.
Our bodies need fatty acid for maintaining healthy and fresh looking skin. Fatty acids also regulate the quality of our skin. Argan oil contains a dozen fatty acids, saturated and unsaturated. Linoleic acid and linolenic acid, essential fatty acids, are present at about 12.7% and 0.34%, respectively. The linoleic acid in argan oil acts as an anti-inflammatory and helps heal damaged skin cells.
Chamomile (Matricaria chamomilla) has UV absorptivity in the spectrum 250-300 nm. Bisabolol (Figure 1) is a monocyclic sesquiterpene alcohol and is the primary constituent of the German chamomile oil. It can effectively stimulate and promote the skin's healing process. It also increases the skin penetration of other cosmetic ingredients, which can be particularly useful when feeding the skin antioxidants. It is known to have anti-irritant, anti-inflammatory and anti-microbial properties (2, 3). Alpha-bisabolol has been shown to reduce UV-induced erythema in-vivo.

COMBINING ANTIOXIDANTS WITH PHYSICAL SUNSCREENS

There exists a fair amount of literature particularly recent with regards to the addition of antioxidants in sunscreen products. For example, a past study with a panel of 32 volunteers found that pomegranate extract added to sunscreen increased the SPF by 20%. Higher SPF products, especially those with effective UVA protection, have become more desirable with increased consumer awareness of the risks associated with harmful UV exposure. It has become widely accepted by consumers that antioxidants can protect against free-radicals and cellular damage.
The goal of our study was to create an antioxidant blend that:

1. Substantially boosts SPF and PFA.
2. Complements inorganic and organic UV filters and is stable and compatible.

We decided to explore a wide range of antioxidants, twenty-two in total, in combination with physical sunscreen dispersions to optimize sun protection in formulations.

One of the issues with combining antioxidants with physical sunscreens is the change in colour that may take place due to oxidation. Micronized titanium dioxide has residual reactivity towards unstable ingredients which may cause degradation leading to discolouration and undesirable odor. A variety of antioxidants and bioactives were tested for their stability with inorganic UV filters (Figure 2).

Figure 2. (The visible colour change of 10 nm, 15 nm, and 60 nm particle size dispersions of titanium dioxide when combined with ascorbyl palmitate).

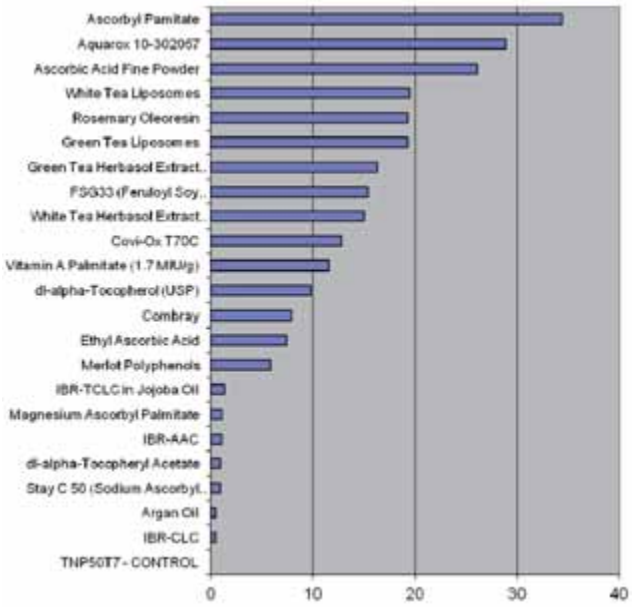

Figure 3. Antioxidants effect on colour change of a titanium dioxide dispersion CIELAB Colour difference after 5 days at room temperature.

A 50% dispersion of 15 nm titanium dioxide in C12-15 alkyl benzoate was prepared and 5% of each antioxidant was added to the dispersion. This was blended together using an Unguator to obtain an intimate mix. We measured the colour with a Datacolour Microflash unit after it was originally made and then followed its progress over several days with measurements (Figure 3).
The large change in the CIELAB measurement is shown in the chart above. We also followed this with a second experiment where we made an entire sunscreen formulation using the titanium dioxide dispersion in combination with each of the twenty-two antioxidants. The colour change was less, but correlated well with the original undiluted experiment.
In addition, we ran in-vitro testing on all of the formulations with antioxidants using PMMA plates on a Labsphere. This also helped us to screen the antioxidants to determine which would be best to achieve optimal UVA/UVB while maintaining stability. Based upon the screening studies noted, two of the most compatible antioxidants were selected, argan oil and tocopheryl acetate. To finalize our mixture we also evaluated anti-inflammatory actives to provide a synergy with skin care properties. Our final blend then consisted of argan oil, tocopheryl acetate, and bisabolol.

Ingredients	Control KSL-171A	Test KSL-171C
% TiO_2	6.0	6.0
% ZnO	4.6	4.6
% Antioxidant Mixture	———	5.0
SPF	31.4	44.9
% Boost	———	43.1%

Table 1. The SPF effect of the antioxidant mixture with inorganic sunscreen actives.

Ingredients	Control KSL-177-CH	Test KSL-177C-CH
% TiO_2	5.8	5.8
% ZnO	3.7	3.7
%Antioxidant Mixture	———	3.6
PFA	7.5	10.1
% Boost	———	35.4%

Table 2. The PFA effect of the antioxidant mixture with inorganic sunscreen actives.

Ingredients	Control KSL-138	Test KSL-138V
% Avobenzone	3.0	3.0
% Homosalate	15.0	15.0
% Octisalate	10.0	10.0
% Oxybenzone	3.0	3.0
% Antioxidant Mixture	———	5.0
SPF	40.9	54.8
% Boost	———	34.0%

Table 3. The SPF effect of the antioxidant mixture with organic sunscreen actives.

Ingredients	Control KSL-228A	Test KSL-228B
% TiO_2	4.05	4.05
% ZnO	11.76	11.76
% Octinoxate	7.5	7.5
% Antioxidant Mixture	———	5.0
SPF	44.0	57.5
% Boost	———	30.7%
Critical Wavelength	373.7	373.8

Table 4. The SPF effect of the antioxidant mixture with mixed organic and inorganic sunscreen actives.

THE EFFECT OF ANTIOXIDANT MIXTURE ON SPF AND PFA

Enhanced photoprotection can be achieved by topically applying an appropriate combination of antioxidants. The effect of topical antioxidants after UV radiation is less obvious, whereas the photoprotective effect of topical antioxidants applied before UV exposure has been well recognized (4). We prepared a number of concentrations of the antioxidant mixture in a water-in-oil sunscreen formulation to better understand its overall effect on SPF and PFA. First, we tested varying concentrations of the antioxidant/botanical mixture at increasing levels. Titanium dioxide was selected as the active to be used with the antioxidant/botanical mixture for this range finding part of the study. We found for that particular base formulation, the concentration leveled off at about 3–5% with its SPF boosting effect. The formulations were tested using the FDA in-vivo method on a small group of people.
The antioxidant/botanical mixture was then tested with inorganic filters alone, organic filters alone, and finally inorganic and organic filters mixed. The inorganic sunscreen formulation was also assessed for PFA.

RESULTS

The antioxidant/botanical mixture, now known as SunBoost ATB™, at a use level between 3.6 to 5.0% in formulations, was able to boost SPF and PFA by 30 to 43%.
Tables 1 through 4 show the concentrations of the sunscreen actives and the SunBoost ATB™ with the results. It is clear that we are able to improve our sunscreen formulation with the addition of the mixture of antioxidants and botanicals.

It was important to assess the colour stability of the finished formulations over time, as well, since mostly all sunscreens are white milky emulsions, gels, sticks or sprays.

CONCLUSION

Reactive oxygen species play a major role in photoaging and degrade proteins in the skin. Inorganic sunscreen actives, such as titanium dioxide and zinc oxide, when combined with select antioxidants help to prevent photoaging. Antioxidants and sunscreen actives need to be compatible and present at the correct ratios in sunscreens to achieve this. We found that tocopherols, both natural and its ester forms, work well together with titanium dioxide.
This was also confirmed by an oxidative stability study by International Flora Technologies using the Ominion Oxidative Stability Instrument (OSI) whereby titanium dioxide combined with tocopherols actually improved the long term stability of botanical oils (5). Multiple antioxidants have a greater effect than single antioxidants with respect to sun protection.

- Antioxidants and bioactive compounds have great ability to boost the UV protection of sunscreen formulas against both UVA and UVB. The boosting effect can be cumulative.
- This blend is highly compatible with inorganic UV filters.
- SPF/PFA boosters of different mechanisms, when used in proper combination, can boost protection multifold. This also helps to reduce the use of actives, improve the skin feel and aesthetics of sunscreen formulations, as well as provide multiple benefits such as anti-aging, anti-irritation, hydration, rejuvenation, and the prevention of ROS formation (6).

Our antioxidant and botanical mixture, SunBoost ATB™ that contains argan oil, Vitamin E Acetate and bisabolol has shown the ability to improve SPF and PFA. It achieves a considerably higher level of protection than the inorganic or organic sunscreen actives without the addition of the antioxidant/botanical additive. This provides the consumer with better protection overall against UVA/UVB rays.

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